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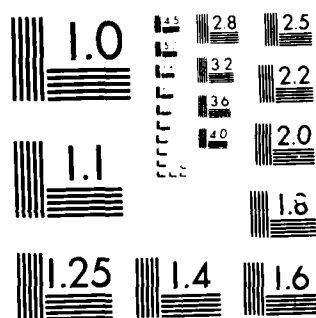
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Data Analysis for Multidimensional Luminescence

by

Sharon L. Neal, Gabor Patonay,
Mark P. Thomas and Isiah M. Warner

Prepared for Publication

in Spectroscopy

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INTRODUCTION

Without exception, spectroscopic methods of chemical analysis exhibit reduced performance in multicomponent analysis because of interference by overlapping component signals. One of the solutions to this problem that chemists in several subdisciplines are currently exploring is the simultaneous evaluation of several sample properties.¹ This approach produces a multidimensional data set that is more characteristic of the sample than the one dimensional data sets generated by evaluating the sample properties separately. Developments in microprocessor controlled instrumentation and multidimensional detectors have reduced the time and effort required to acquire multidimensional data and increased the practicality of multiparametric analysis. However, in order for multiparametric analyses to approach the efficiency of single parameter measurements, data analysis methods capable of efficiently generating and accurately interpreting the results are needed. Multiparametric data analysis is usually composed of three phases: 1)rank analysis which is the determination of the number of sample components, 2)qualitative analysis and 3)quantitative analysis. Moreover, multiparametric techniques often provide superfluous information. Therefore, optimum data reduction methods are needed to extract the salient features of the data for component analysis.

This article reviews data analysis and reduction methods as applied to multidimensional luminescence measurements(MLMs). This format precludes an exhaustive review of the algorithms developed for multiparametric data analysis, but it is our hope that the methods presented here will provide a survey of the kinds of analyses available for all types of multidimensional data. Luminescence (fluorescence and phosphorescence) measurements, in particular, are suited to this kind of analysis because all luminescence measurements are inherently multiparametric.² For example, the intensity of fluorescence (I_f) generated by

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mization methods, which is illustrated by qualitative analysis of multicomponent excitation-emission matrices using the simplex algorithm.

LINEAR METHODS

The utility of acquiring luminescence data in multidimensional format was first recognized by Weber.⁶ In his work, the intensity of luminescence was acquired as a function of multiple excitation and emission wavelengths. This format is now called the excitation-emission matrix (EEM). There are three fundamental properties of luminescence that make this kind of analysis possible: 1) the emission profile of a pure sample is independent of the excitation wavelength, 2) the excitation profile of a pure sample is independent of the monitored emission wavelength and 3) at low absorbances, the intensity of luminescence is directly proportional to the absorbance of the sample. As a result of properties 1 and 2 the rows of an EEM of a pure sample are multiples of the emission spectrum and the columns are multiples of the excitation spectrum. Therefore, a one component EEM can be expressed by the product of two vectors representing the excitation and emission spectra of the sample.

$$M = \alpha xy \quad (1)$$

where α is a concentration dependent scalar. Matrices, such as this, with independent variables plotted on both axes are called bilinear. An example of a non-bilinear matrix is one whose rows are the absorbance spectra of a set of solutions with randomly varying relative concentrations of a set of components. The rows would be linear combinations of the absorbance spectra, the columns would have no physical significance. Figure 1 which shows isometric and contour plots of perylene, illustrates these properties.

As a result of the third property and Beer's law, the EEM of an n component mixture is the sum of the EEMs of the pure components, provided that there are

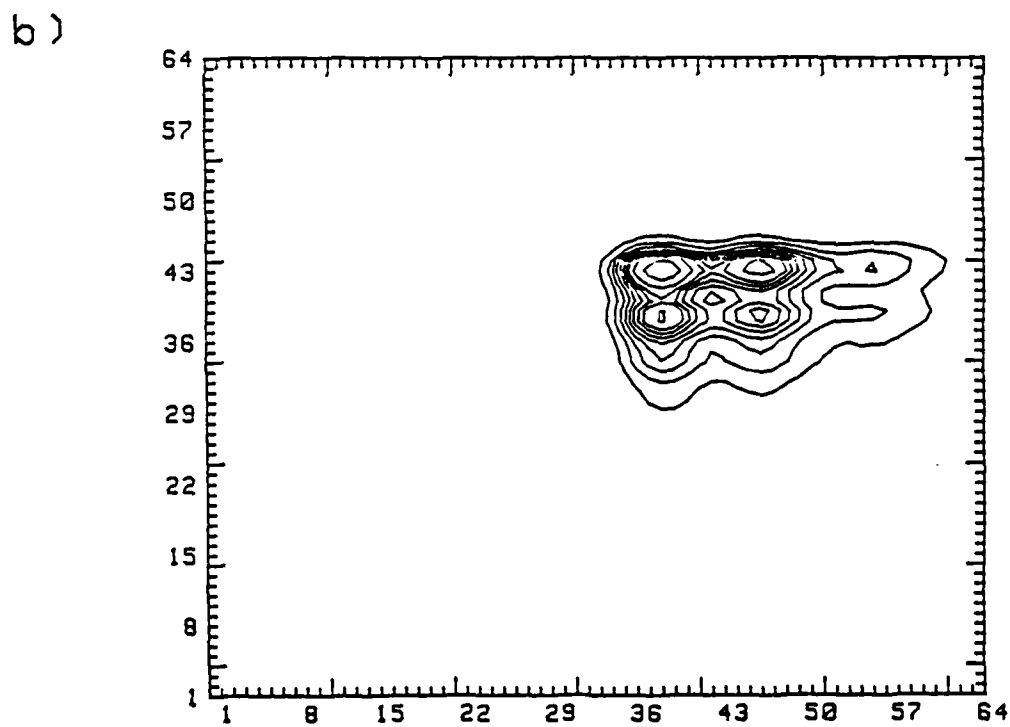
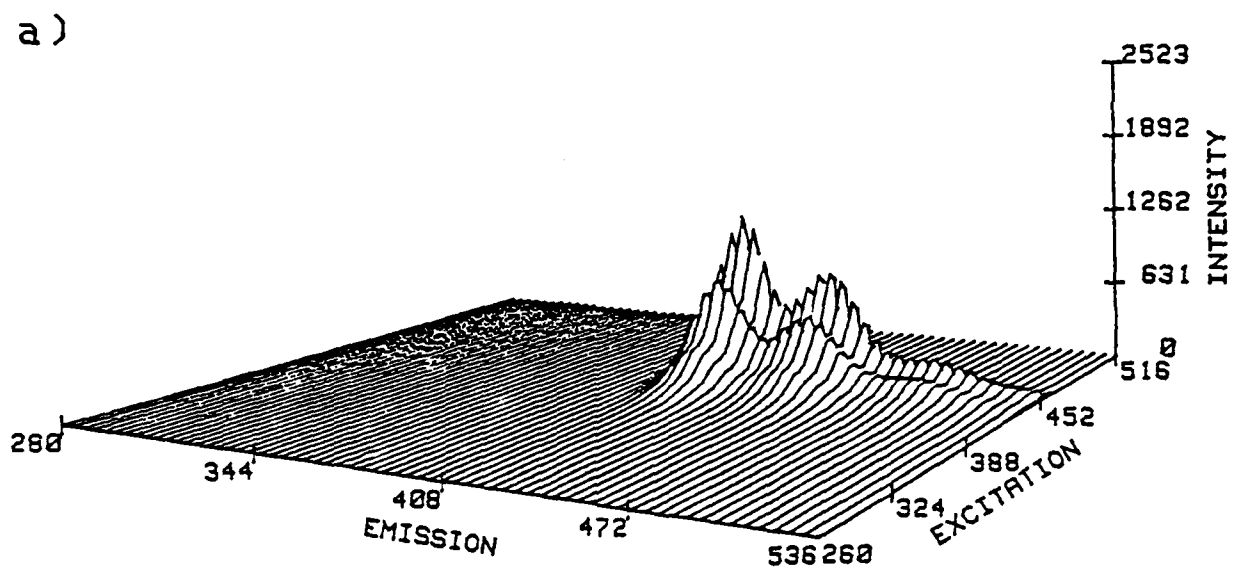


Figure 1

no synergistic effects such as energy transfer. Therefore, the rows of the multicomponent EEM are linear combinations of the emission spectra of the components.

$$x = c_1 x_1 + c_2 x_2 + \dots + c_n x_n. \quad (2)$$

Likewise, the columns of a multicomponent EEM are linear combinations of the component excitation spectra.

$$y = c_1 y_1 + c_2 y_2 + \dots + c_n y_n. \quad (3)$$

The matrix M is represented by

$$M = \sum_{i=1}^n \alpha_i x_i y_i \quad (4)$$

in vector notation where the subscript i denotes each luminescing component. The EEM can be represented more succinctly in matrix notation:

$$M = XY \quad (5)$$

where X is a matrix whose columns are the excitation spectra of the components and Y is a matrix whose rows are the emission spectra of the components. This kind of linear relationship also applies to other luminescence parameters because they are regulated by Beer's law due to their relationship to the luminescence intensity. For this reason, linear methods are also suitable for other forms of matrix-formatted luminescence data.

One of the simplest approaches to the analysis of matrix formatted luminescence data is to use approximations to decompose the matrix into row and column factors.⁹ Knorr and Harris⁷ have applied this method to the fluorescence decay-emission matrix. Independent first order decay is assumed for each component in the sample. A trial time matrix whose rows were generated by convoluting the decay curves corresponding to estimated lifetimes with the instrument response function is formed. Then, the trial time matrix, T, is used to generate

the corresponding spectral matrix. The psuedo-inverse of T' , which is given by $(T'T'T)^{-1}$, is used to extract the spectral vectors from the data matrix when they are not orthogonal to the decay curves on the columns of T . So the spectral matrix is given by

$$A' = LT'T'(T'T'T)^{-1} \quad (6)$$

The model matrix L' is generated by multiplying A' and T' . The elements of T' are adjusted until the squared error between L and L' is minimized.

Matrix decomposition is useful whenever it is possible to make reasonable estimates of one of the experiment parameters. However, if nothing is known about the sample response to changes in either of the experiment parameters, factor analysis based algorithms are more appropriate. Factor Analysis (FA), extracts the smallest set of independent vectors which account for the variance in the data matrix.¹⁰ These independent vectors are called the singular vectors of M or the eigenvectors of the covariance or second moment matrices of M . The MLM can also be expressed as the product of the row and column singular vectors:

$$M = \sum_{i=1}^n a_i u_i v_i \quad (7)$$

where i again denotes the luminescing components. In matrix notation, M can also be expressed as the product of the orthogonal matrices U and V whose rows and columns, respectively, are the singular vectors of M .

$$M = U \Sigma V \quad (8)$$

The diagonal elements of the matrix Σ are the singular values of M , whose magnitudes reflect the significance of the corresponding singular vector to the total variance of the data matrix. When M is ideal, the rank of the matrix is the minimum number of luminescent components contributing to the data. When M is an experimental matrix with random errors superimposed upon the data, the rank

of the matrix is the number of observations made along the shorter axis. In this case, the number of luminescing components in the data is obscured. Several rank analysis methods have been developed to determine the number of components in experimental matrices. The performance of rank analysis procedures on MLMs has been compared in a recent paper by Rossi and Warner¹¹ which reported the development of a frequency domain rank analysis method. When the number of luminescing components is correctly determined, the product of the singular vector matrices provides a least squares approximation to the data.¹⁰

The presence of random noise in the data is a serious consideration in data analysis. As in the case of rank analysis, the presence of random noise reduces the performance of most data analysis methods. Often it is possible to avoid this problem by using more concentrated samples, signal averaging or a combination of both of these methods. The performance of some data analysis methods can also be improved by the use of time¹² or frequency¹³ domain digital filtering methods which have been designed to reduce noise by mathematically discriminating between noise and spectral information.

When M is an EEM, U and V are excitation and emission singular vector matrices, respectively. The singular vectors and spectra span the same vector space and, are therefore linear combinations of each other. There must be, then, a matrix K whose elements are the coefficients used to express the spectra in terms of the singular vectors.

$$X = UK \quad (9)$$

Since M is the product of U and V , changes in U require complementary changes in V . Therefore,

$$Y = K^{-1}V. \quad (10)$$

The goal of FA spectral resolution algorithms is to determine the values of K and K^{-1} that transform U and V to X and Y .

In 1977, Warner *et al.* reported the development of a FA based algorithm for the resolution of binary EEMs.¹⁴ This algorithm is an extension of Self Modeling Curve Resolution¹⁵ to bilinear non-negative matrices. The singular vectors will generally be forced to contain negative elements in order to achieve orthogonality. The values of the elements of K and K^{-1} are found by solving the expressions for the transformed vectors under the condition that they are non-negative, as are true excitation and emission spectra. The expressions for the non-negativity constraints are given by

$$UK \geq 0 \quad (11)$$

and

$$K^{-1}V \geq 0 \quad (12)$$

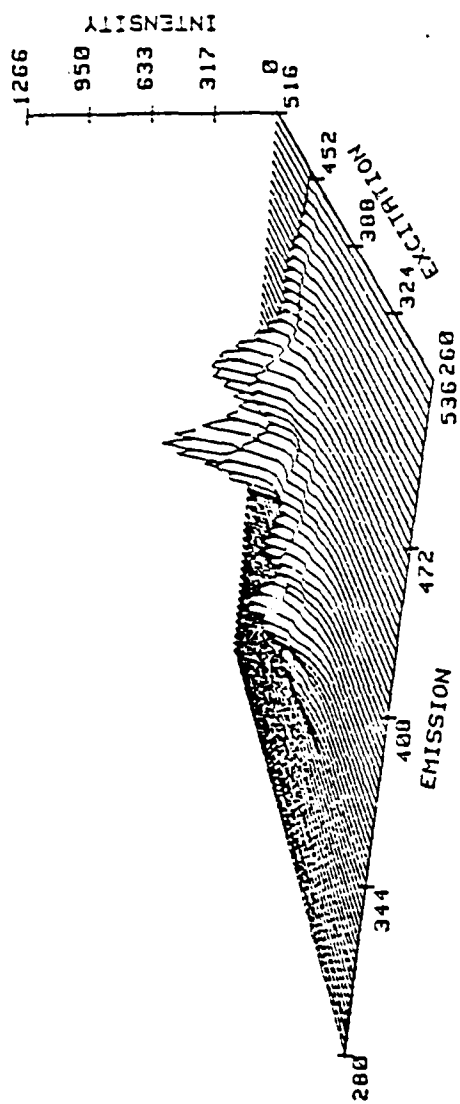
in matrix format. Solving these equations for the elements of K generates the following ranges for the elements of K :

$$\min_{v(2)_j > 0} \frac{v(1)_j}{v(2)_j} \geq k_{12} \geq \max_{u(1)_i > 0} \frac{-u(2)_i}{u(1)_i} \quad (13)$$

and

$$\min_{v(1)_j > 0} \frac{v(2)_j}{v(1)_j} \geq k_{21} \geq \max_{u(2)_i > 0} \frac{-u(1)_i}{u(2)_i} \quad (14)$$

For simplicity, the values of k_{11} and k_{22} are considered to be unity. The ranges for k_{12} and k_{21} converge when the compounds, whose spectra are represented by the variables in the numerators, are sole absorbers or emitters at the wavelengths represented by i and j . This convergence produces unambiguously correct transformations. Figure 2 is an isometric plot of an EEM of an anthracene/perylene mixture and the singular vectors and spectra resolved from it. The spectra are completely resolved because the spectra of both components are sole contributors to the matrix at characteristic excitation and emission wavelengths.



b)

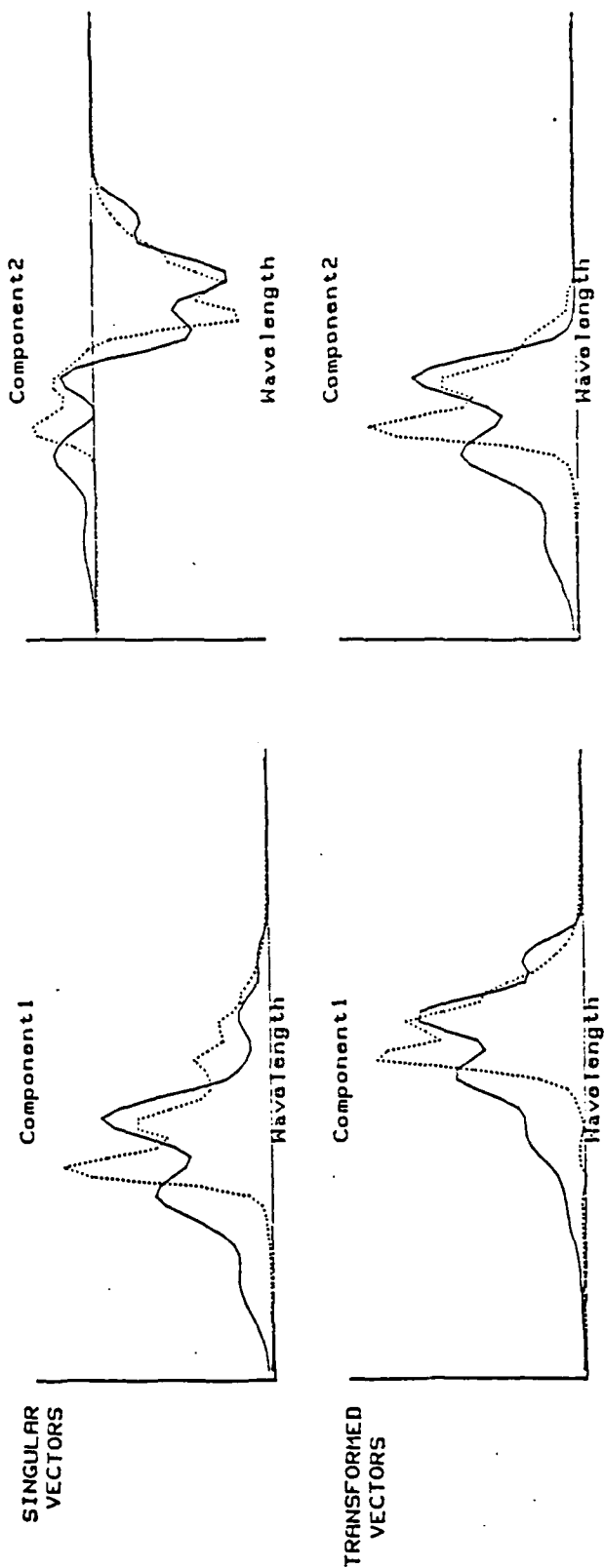


Figure 2

Since 1977, two other FA based spectral resolution algorithms have been developed for MLM. One is suitable for resolving binary matrices that are not bilinear or not subject to non-negativity constraints along one axis.¹⁶ The other is capable of resolving the spectra of components from non-bilinear data matrices of higher order mixtures.¹⁷

Factor Analysis algorithms have not yet been developed which can resolve spectra from data matrices when none of the components is a sole emitter or absorber. Moreover, in most cases, the analyst does have some prior knowledge of the sample components. In instances where the objective is quantitative rather than qualitative analysis, Linear Least Squares Analysis is appropriate.¹⁸

A mixture matrix whose components are known but have unspecified concentrations can be represented as

$$M = \sum_{i=1}^n c_i M_i \quad (15)$$

where M_i is the standard matrix of the i th component and c_i is the ratio of the sample concentration to the standard concentration of the i th component. The best least squares approximation of M has a minimum squared error, where the error matrix E is given by

$$E = M - \sum_{i=1}^n c_i M_i \quad (16)$$

and the weighted sum of the squared elements of E is a minimum given by

$$\sum_{kl} t_{kl} e_{kl}^2 = \sum_{kl} t_{kl} (m_{kl} - \sum_i c(i) m(i)_{kl})^2 = \min \quad (17)$$

where e_{kl} is the element on the k th row and l th column of the error matrix, m_{kl} is the kl th element of the observed data matrix, $m(i)_{kl}$ is the kl th element

of the i th standard matrix, $c(i)$ is the concentration of the i th standard matrix, and the t_{kl} are the weighting factors for the elements of E . The weighting factors reflect the dependence of the variance in each matrix element on the magnitude of the signal. For photon limited noise, the inverse of the signal is a suitable weight. Differentiating equation 17 with respect to concentration defines the least squares condition:

$$\sum_j \left[\sum_{kl} t_{kl} m(i)_{kl} m(j)_{kl} \right] c(j) = \sum_{kl} t_{kl} m(i)_{kl} m_{kl} \quad (18)$$

If the terms in equation 18 are grouped by subscripts, the expression can be represented in matrix format:

$$Wc = p \quad (19)$$

where W is the n by n matrix whose elements represent the terms given by $\sum_j [\sum_{kl} t_{kl} m(i)_{kl} m(j)_{kl}]$, c is a vector whose elements are the $c(j)$ and p is a vector whose elements are given by $\sum_{kl} t_{kl} m(i)_{kl} m_{kl}$. The values of the $c(j)$ can be found from this equation using the inverse of W :

$$c = W^{-1}p \quad (20)$$

The variances associated with the $c(j)$ are given by

$$\sum_{kl} t_{kl}^2 \left\{ \left[\sum_r w_{ir}^{-1} m(r)_{kl} \right]^2 \sigma_{(m_{kl})}^2 + \sum_j \left[e_{kl} w_{ij}^{-1} - \left(\sum_r w_{ir}^{-1} m(r)_{kl} \right) c(j) \right]^2 \sigma_{[m(i)_{kl}]}^2 \right\} \quad (21)$$

where $\sigma_{(m_{kl})}$ is the estimated variance of the data matrix and $\sigma_{[m(i)_{kl}]}$ is the estimated variance of the i th standard matrix. Table 1 shows the results of the quantitative analysis of a nine component mixture of polynuclear aromatics using least squares analysis.

Other quantitative analysis methods have been developed for MLMs. Ratio deconvolution is an algebraic method which uses the average ratios of the unknown and standard matrices to separate multicomponent EEMs into their compo-

Table I. Quantitative Analysis of a Nine-Component Mixture*

component	relative concentration	least squares concentration
naphthalene	1.485	1.465
carbazole	0.939	0.944
fluorene	1.180	1.176
phenanthrene	1.376	1.383
anthracene	1.311	1.309
pyrene	0.678	0.678
chrysene	1.406	1.407
perylene	0.899	0.900
fluoranthene	0.568	0.568

* Copied from reference 28.

nent matrices.^{19,20} Rank annihilation is a factor analysis based method which verifies the presence of a component by the loss of a principle component when a suitable amount of the compound is subtracted from the data matrix. Rank annihilation procedures have been developed for two dimensional^{21,22} and three dimensional²³ systems using calculations in reduced space to reduce the number of computations performed.²⁴

FOURIER METHODS

Many of the linear methods are data reduction methods that exploit the additional information in a multidimensional data set to extract the more familiar one dimensional spectra. However, in order to take full advantage of multidimensional data, data analysis methods that actually analyze the data in both dimensions are needed. Ratio deconvolution is an example of a linear time domain method that uses the entire matrix for analysis. The fact that frequency domain methods have a limited ability to separate spectral contributions from noise, gives them a particular suitability for this kind of analysis. To date, the frequency domain methods that have been developed for MLMs have been developed for the EEM. Correlation analysis in the frequency domain has been chosen for analysis of EEMs because of its relative insensitivity to phase differences and background fluctuations between data matrices. Moreover, the maximum values in frequency domain auto-correlation functions are weighted in favor of signal as opposed to random noise because of the predominance of low frequency components in spectral information.²⁵ Correlation analysis or spectral matching methods compare the data matrix to a library of standard matrices. The identity of the sample is postulated based on the degree of similarity to those standards.

A global perspective of the data is provided by viewing the data as an image or two dimensional function rather than a vector product. Therefore, it's more convenient to describe the data matrix M as

$$M = f(x,y). \quad (22)$$

where x and y are variables representing the excitation and emission wavelengths. In the time domain, the correlation of the data matrix and the library standards is given by

$$f(x,y) \circ g(x,y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(\alpha,\beta) g(x+\alpha, y+\beta) d\alpha d\beta \quad (23)$$

where α and β are shift parameters and \circ denotes convolution. This function is much easier to evaluate in the frequency domain where

$$f(x,y) \circ g(x,y) \leftrightarrow F(u,v) G^*(u,v). \quad (24)$$

The symbol " \leftrightarrow " represents a Fourier transform pair and $*$ denotes the complex conjugate. The capitalized functions are the frequency domain counterparts of the data and standard matrices. The relationship between the time and frequency domain functions is given by

$$F(u,v) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x,y) \exp[-2\pi i(xu+yv)] dx dy \quad (25)$$

where x and y are time domain coordinates and u and v are frequency domain coordinates.

Rossi and Warner have developed a novel pattern recognition algorithm for the EEM which evaluates the spectral match in the frequency domain.²⁶ Since any auto-correlation function, i.e. the correlation of any two identical functions, is even, real and positive, the sum of the imaginary coefficients and negative real coefficients of the correlation of a match should be zero. They also report

the use of a third frequency domain evaluation parameter, which is not related to correlation analysis, the intervector distance. The intervector distance, D , is given by

$$D = \left[\sum_i \sum_j (R(i,j) - R'(i,j))^2 + (I(i,j) - I'(i,j))^2 \right]^{\frac{1}{2}} \quad (26)$$

where $R(i,j)$ and $I(i,j)$ are the real and imaginary coefficients of the transformed data matrix and $R'(i,j)$ and $I'(i,j)$ are the real and imaginary coefficients of the library standard. When two data matrices match, D should equal zero. Table 2 and Figure 3 show the match parameters and fluorescence emission and excitation spectra of three anthracene derivatives, respectively. This example shows that correlation analysis is able to differentiate compounds with very similar spectra.

Correlation analysis has also been used for quantitative analysis of EEMs.²⁷ The concentration of a sample, relative to that of the standard, is given by

$$\bar{x} = s \circ f(0,0) / s \circ s(0,0) \quad (27)$$

where $s \circ f(0,0)$ is the maximum intensity of the correlation of the unknown and the standard and $s \circ s(0,0)$ is the auto correlation of the standard. For multi-component EEMs

$$f(x,y) = \sum_i f_i(x,y) \quad (28)$$

and

$$\bar{x}_i = f \circ s_i(\alpha_i, \beta_i) / s \circ s'(\alpha_i, \beta_i) \quad (29)$$

where $f \circ f_i(\alpha_i, \beta_i)$ is the intensity of the correlation of the unknown and the standard at the coordinates where the maximum intensity of the auto-correlation of the i th component occurs and $s \circ s'(\alpha_i, \beta_i)$ is the maximum intensity of the correlation of the standard with a standard of the i th component matrix. Table

3 shows the known and calculated concentrations of 9,10 dimethyl anthracene in a series of solutions of polynuclear aromatic hydrocarbons.

OPTIMIZATION METHODS

In many applications, optimization methods are used to direct the execution of other algorithms. This is also the case in the application of optimization procedures to MLM analysis. As mentioned in the section on linear methods, rank annihilation procedures quantify sample components by determining the concentration of the component needed to reduce the rank of the matrix by subtraction of that component. An alternative procedure for this method is to use the simplex algorithm, a linear programming technique, to minimize the singular value associated with the analyte rather than least squares.²⁸ The quantitation of an r component EEM can be expressed as the maximization of Γ where

$$\Gamma = \sum_i^r a(i)c(i) \quad (30)$$

where $a(i)$ is given by

$$a(i) = \sum_{kl} m(i)_{kl} \quad (31)$$

subject to the constraints that

$$e_{kl} \geq 0 \quad (32)$$

and

$$c(i) \geq 0 \quad (33)$$

where m_{kl} is the kl th element of the data matrix, $m(i)_{kl}$ is the kl th element of the i th standard matrix and $c(i)$ is the concentration of the i th component in the data matrix. The values of m_{kl} and $m(i)_{kl}$ are fixed, so the algorithm adjusts the values of the $c(i)$ until the constraints in equations 32 and 33 are met. Table

Table III. Quantitative Analysis of 9,10-dimethyl anthracene solutions*

	known conc.	correlation intensity	calc. conc.	%error
Standard #1	9.94×10^{-6}	165520		
Standard #2	1.99×10^{-6}	35432		
Standard #3	9.94×10^{-8}	1893		
Standard #4	5.96×10^{-8}	1229		
Unknown #1	1.78×10^{-5}	282799	1.70×10^{-5}	4.51
Unknown #2	1.78×10^{-6}	31622	1.78×10^{-6}	.23
Unknown #3	1.78×10^{-7}	3361	1.77×10^{-7}	.56
Unknown #4	1.78×10^{-8}	376	1.82×10^{-8}	4.00

* Copied from reference 27.

4 compares the results of a the simplex directed quantitation of the nine component mixture of polynuclear aromatic hydrocarbons that was also evaluated by least squares and reported in Table 3.

CONCLUSIONS

Algorithms for all phases of multidimensional luminescence data analysis, (rank, qualitative and quantitative analysis) have been described. Data reduction methods which compress multidimensional data sets into more manageable formats were also discussed. This survey showed that linear algebra, Fourier transform and optimization techniques have been applied to the analysis of multidimensional luminescence data. The frequency of their use indicates that linear time domain methods are still preferred, but the other methods are beginning to receive increased attention. This is particularly true with frequency domain methods which have seen the largest increase in use in recent studies. Another area of special interest are the factor analysis spectral resolution algorithms which can resolve sample component spectra without prior knowledge of the component identities. However, these methods have limited utility because of the requirement that all resolved components be sole absorbers or emitters in some segment of the wavelength region scanned. Optimization methods have been least developed to date, but their number should increase as research in digital data analysis continues. As would be expected, quantitative analysis methods are better developed than qualitative analysis methods since they usually require that the number and identity of the analyte(s) be known. Developments in qualitative analysis methods should increase as demand for new quantitative analysis methods decreases due to the availability of efficient algorithms.

This review of data analysis for multidimensional luminescence was presented not only because its development parallels that of other multiparametric data an-

Table IV. Quantitative Analysis of a Nine-Component Mixture*

component	relative concentration	simplex concentration
naphthalene	1.485	1.493
carbazole	0.939	0.951
fluorene	1.180	1.194
phenanthrene	1.376	1.356
anthracene	1.311	1.303
pyrene	0.678	0.693
chrysene	1.406	1.396
perylene	0.899	0.886
fluoranthene	0.568	0.566

* Copied from reference 28.

alyses, but also to promote interest and continued research in the multidimensional approach. Many of these methods are directly applicable to other kinds of multiparametric data. It is certain that as these methods are more widely used and become more familiar, the range and difficulty of problems to be addressed will continue increase.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Figure 1. a) Isometric and b) contour plots of the EEM of 1.1×10^{-6} M perylene.

Figure 2. a) Isometric plot of the EEM of 7.5×10^{-6} M anthracene and 5.5×10^{-7} M perylene. b) The singular vectors and spectra resolved from this matrix.

Figure 3. a) Emission spectra of 2-t-butylanthracene, 2-methylanthracene, and 2-ethylanthracene acquired with excitation at 361 nm. b) Excitation spectra of these compounds acquired with emission at 407 nm.

BIOGRAPHIES

Sharon L. Neal received her BS degree from Spelman College in Atlanta, Georgia in 1980. After working for two years as an analytical chemist for the Coca-Cola Co., also in Atlanta, she joined the research group of I. M. Warner. She is presently completing work for the PhD, concentrating her research efforts on the development of new digital analysis methods for multidimensional data.

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Isiah M. Warner received his BS degree from Southern University in Baton Rouge in 1968 and his PhD from the University of Washington in 1977. He worked as a research chemist at Battelle Northwest in Richland, Washington from 1968 to 1973. He is presently associate professor of chemistry at Emory University in Atlanta, Georgia. His current research interests include molecular absorption,

a sample is a function of the emitted light wavelength as well as the exciting (absorbed) light wavelength. The luminescence properties commonly used for chemical analysis are excitation wavelength, λ_{ex} , emission wavelength, λ_{em} , luminescence lifetime, τ_l and luminescence polarization, often denoted by the anisotropy, r_l . In addition to these commonly used parameters, luminescence has been used to detect chromatographic separations³, denoted by the retention time, t_r , circular dichroism bands⁴, denoted by the luminescence ellipticity, θ_l , and the luminescence phase angle⁵, denoted by ϕ .

A multidimensional luminescence measurement can be generated by evaluating the intensity of luminescence (I_l representing I_f or I_p) with respect to two or more of these parameters. In practice, most MLMs are produced by varying two parameters so that the resulting graphical representations can be displayed in a three dimensional format. The luminescence data matrices that have been reported are the excitation-emission matrix⁶ where $I_l = f(\lambda_{ex}, \lambda_{em})$, the fluorescence ellipticity matrix⁴ where $I_f = f(\theta_f, \lambda_{em})$, the fluorescence decay - emission matrix⁷ where $I_f = f(\tau_f, \lambda_{em})$, the fluorescence decay - excitation matrix⁸ where $I_f = f(\tau_f, \lambda_{ex})$, and the retention time - emission matrix³ where $I_f = f(t_r, \lambda_{em})$. One notable exception to this convention is the acquisition of synchronously scanned luminescence as a function of the phase angle.⁵ In this measurement, I_f is a function of λ_{ex} , λ_{em} , and ϕ but the graphical representation of the data is three dimensional.

The data analysis methods developed for MLM will be presented in three groups. The first group consists of Linear Methods. The techniques in this class use linear algebraic methods to perform rank, qualitative and quantitative analysis. The second group is comprised of Fourier methods, specifically correlation analysis, to characterize and quantify sample components. The last group

and luminescence spectroscopy, development of novel analytical instrumentation and the reduction and interpretation of multicomponent chemical data.

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